



6th International SPMD Workshop And Symposium

July 25-27, 2000

Hosted by:

USGS Columbia Environmental Research Center
Columbia, Missouri, USA

AGENDA

Monday July 24th –

6:00 PM – 9:00 PM **Welcome Reception:** Join us as you arrive in town for an evening of good food, drink, and camaraderie. This is a great opportunity to relax after your long trip and make some new acquaintances or meet some old friends. A complementary shuttle will depart the Hampton Inn for the reception every half hour (sponsored by EST).

Tuesday July 25th –

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| 8:00 AM | Registration and poster set-up |
| 9:00 AM | Introduction and Opening Remarks – J. Petty |
| 9:30 AM | <i>Considerations Involved with the Use of Semipermeable Membrane Devices (SPMDs) For Monitoring Environmental Contaminants</i> – J. Petty, C. Orazio, J. Huckins, R. Gale, J. Lebo, J. Meadows, W. Cranor, D. Alvarez, K. Echols |
| 10:00 AM | <i>Evaluation of Persistent Hydrophobic Organic Compounds in the Columbia River Basin Using Semipermeable Membrane Devices</i> – K. McCarthy and R. Gale |
| 10:30 AM | Break |
| 10:45 AM | <i>Mussels, SPMDs and other Passive Samplers in Dutch Coastal Waters</i> – K. Booij |
| 11:15 AM | <i>Monitoring of POPs in Odra River (Czech Republic) by Passive Methods (SPMD, DGT)</i> – T. Ocelka, K. Czajka, R. Grabic, M. Cizkova, J. Stecka |
| 11:45 AM | Catered Lunch |
| 1:30 PM | Posters Session – Posters will remain hanging throughout the workshop. This session will allow for questions and answers between the presenters and attendees. |
| 3:00 PM | Break |
| 3:15 PM | <i>Investigation of Dissolved Polycyclic Aromatic Hydrocarbons in Waters of the Everglades</i> - S. Haynes, R. Gragg, C. Orazio, J. Lebo, J. Petty, J. Huckins, W. Cranor, R. Clark |
| 3:45 PM | <i>Semipermeable Membrane Devices (SPMDs) used for evaluation of concentration profiles of pyrethroids in ponds</i> – B.B. Mogensen, P. Sørensen, F. Stuer-Lauridsen, P. Lassen |
| 4:15 PM | <i>Removal of Methyl Oleate from SPMD extracts using Normal-Phase SPE</i> – K. Gustavson |
| 4:45 PM | Closing Comments |
| 5:00 PM | End for the Day |

6:00 PM Social Gathering at Les Bourgeois Winery overlooking the Missouri River and surrounding Bluffs

Wednesday July 26th –

9:00 AM *A Holistic Approach for Assessing the Presence and Potential Impacts of Environmental Contaminants – J. Petty, J. Huckins, W. Brumbaugh, D. Alvarez, W. Cranor, J. Lebo*

9:30 AM *Development of Two Passive Integrative Samplers for Toxic Trace Metals: The PIMS and SLMD – B. Brumbaugh, J. Petty, J. Huckins, T. May*

10:00 AM *Current Status in the Development of an Integrative Sampler for Polar Organic Chemicals in Water – D. Alvarez, J. Petty, J. Huckins, S. Manahan, C. Rostad, E. Furlong, T. Leiker, S. Werner, A. Rastall*

10:30 AM Break

10:45 AM *Quality Assurance/Quality Control Considerations for the Processing and Analysis of SPMD Samples – W. Cranor, J. Petty, J. Huckins, D. Alvarez, R. Clark*

11:15 AM *Looking at SPMD Results from a Different Angle – K. Booij*

11:45 AM Lunch

1:30 PM *Toxicological Monitoring of a Simulated Oil Spill on the St. Lawrence River: Phytoremediation – B.T. Johnson, J. Petty, J. Huckins, K. Lee, J. Gauthier, A. Venosa*

2:00 PM *The Use of Passive Samplers to Determine Soil Contaminant Levels and Monitor Changes in Contaminant Bioavailability with Aging – K. Johnson, C. Friedel, T. Kress*

2:30 PM *Using Semipermeable Membrane Devices for Estimating the Bioavailability of Organic Chemicals in Soil – J. Wells, R. Lanno*

3:00 PM Break

3:15 PM Open Discussion Period

4:45 PM Closing Comments

5:00 PM End of the Day

6:00 PM Evening Dinner and Social Gathering at Bethel Park. Cool, casual clothing for this outdoors event is recommended. Hopefully the weather will cooperate.

Thursday July 27th –

9:00 AM Open Discussion, Questions and Answers of Topics of Interest

11:30 AM End of Workshop – Have a safe trip home.

Dress is informal. We wish this to be a relaxed atmosphere where everyone can be comfortable and participate wholeheartedly in the discussions.

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ABSTRACTS

PLATFORM PRESENTATION

Current Status in the Development of an Integrative Sampler for Polar Organic Chemicals in Water

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The ability to monitor aquatic environments for polar organic contaminants (i.e., pesticides, pharmaceuticals, etc.) has recently become a topic of considerable interest. Many of these chemicals, although typically not bioconcentratable, have been linked to acute toxicity and chronic sublethal effects such as endocrine disruption. A prototype sampling device was developed and has been demonstrated to integratively sample model polar organic contaminants such as 17 α -ethynylestradiol, diazinon, and atrazine for up to 28 days in a laboratory setting. The sampling device consists of a mixture of polymeric solid-phase extraction resins within a hydrophilic membrane enclosure. A proof-of-concept field deployment was utilized to demonstrate the ability of the POCIS to perform under actual environmental conditions. Following a 28 day deployment in a wetland complex consisting of treated effluent from a municipal wastewater treatment facility and water from the Missouri River, qualitative identification of a variety of compounds was achieved. Tentatively identified compounds include among many others: atrazine, hydroxyatrazine, ibuprofen, ethynylestradiol, nonyl phenol, and caffeine. The atrazine sequestered from the Missouri River distribution channel was at a concentration amenable for quantitation. Using the calculated sampling rate for atrazine under more turbulent conditions, the ambient water concentration was estimated to be 0.84 ppb, which is in agreement with the reported atrazine concentration in the Missouri River of 1.16 ppb from 3 months earlier. Extracts submitted to a Yeast Estrogen Screen (YES) to determine the estrogenic potential sequestered chemicals produced highly significant responses indicating the presence of one or more estrogenic compounds in the complex mixtures.

PLATFORM PRESENTATION

Looking at SPMD Results from a Different Angle

K. Booij

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SPMDs are great for identifying sources of contamination on small geographical and temporal scales, i.e. when in the study area the water flow velocities and the exposure temperatures are essentially the same. A higher absorbed amount for a particular compound usually indicates a higher exposure concentration. Things become more complicated, however, when between-compound comparisons have to be made. E.g. low K_{ow} compounds may have higher aqueous concentrations, and yet have smaller absorbed amounts because the SPMD sorption capacity is limiting. Another complication arises when substantial between-site differences exist in water flow velocities and temperatures. A third difficulty that we have to deal with is that the “SPMD absorbed amount” is not a quantity that is easy to use in environmental fate modeling and in monitoring programs. Unless we can establish a firm link between the absorbed amounts and the aqueous concentrations people will always scratch their heads and wonder what these numbers really mean.

The use of Performance Reference Compounds (PRCs) helps to identify and eliminate these problems. Starting from the Huckins *et al.* 1993 and 1999 models I plan to elaborate on equilibrium versus kinetic modeling. Then I will show some recent calibration data for chlorinated hydrocarbons and PAHs (combined uptake and PRC dissipation data). It appears that *in situ* sampling rates (L/d) can be calculated from PRC dissipation rate constants (d^{-1}) and SPMD-water partition coefficients (K_{sw}) for the PRCs. This approach eliminates the need for making uptake calibration experiments in the lab. The only data we need in order to calculate aqueous concentrations is: K_{sw} data for a number of PRCs ($10^4 < K_{ow} < 10^6$) and K_{sw} data for all low K_{ow} analytes ($< 10^5$) we want to study.

PLATFORM PRESENTATION

Mussels, SPMDs and other Passive Samplers in Dutch Coastal Waters

K. Booij

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SPMDs, LPDE membranes and mussels were exposed for six weeks at four to five stations in the Scheldt estuary and in the Southern North Sea around February and around October 1999.

Mussel results were a major disaster as far as the between-site contamination assessment was concerned. The dissipation rate constants of the Performance Reference Compounds indicated that the effect of flow differences on the sampling rates was smaller than 30%. Equilibrium was attained for low K_{ow} compounds ($<10^5$).

Additional field experiments were carried out in the Western Wadden Sea. SPMD exposure under controlled forced flow conditions did not really pay off. Sampling rates increased by a factor of two, but the time efforts needed to maintain the forced flow were quite large. Passive sampling using silicone tubing yielded dramatically increased amounts of low K_{ow} compounds ($<10^5$), indicating that low sorption capacity may limit the number of compounds that we can identify in the field.

PLATFORM PRESENTATION

Development of Two Passive Integrative Samplers for Toxic Trace Metals: The PIMS and SLMD

W. Brumbaugh, J. Petty, J. Huckins, and T. May

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Two passive integrative membrane samplers, one designed for sampling neutral Hg species in air or water, and the other for sampling divalent metal ions from water, (e.g., Cd, Co, Cu, Ni, Pb, Zn) have been successfully developed. The passive integrative mercury sampler or PIMS (U.S. patent granted) is primarily suited for sampling gaseous elemental Hg from air and it may be deployed for intervals of at least 90 days. It is anticipated that the PIMS will be useful for monitoring of mercury emission sources, measuring neutral Hg species in both air and water in cycling studies, and for assessing exposure levels in the laboratory and workplace. The stabilized liquid membrane device or SLMD (U.S. patent pending) is suitable for either *in situ*, integrative water sampling, or for the determination of labile metal ion species in grab water samples. Design characteristics and experimental field data will be presented and discussed for each sampler.

PLATFORM PRESENTATION

Quality Assurance/Quality Control Considerations for the Processing and Analysis of SPMD Samples

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While a significant body of data exists in the peer-reviewed literature regarding the use of SPMD samplers for sequestering environmental organic contaminants, there is less data available in this same literature regarding the data quality during the processing of SPMDs and the analyses of contaminants so sequestered. The “Quality Objective” for the chemical analyses of contaminants sequestered by SPMDs is first, to achieve acceptance of analytical data from SPMDs by scientific peer-review, and ultimately to achieve acceptance of SPMD data by regulatory authority. Scientists at the USGS Columbia Environmental Research Center have recently compiled, within an established Quality Assurance Program (QAP) and under the control of an approved Quality Assurance Project Plan (QAPP), data that will be presented as the foundation of a data base to establish “Control Limits” associated with SPMD processing and analyses. These control limits will be tied to other Quality Control (QC) parameters associated with the use and analysis of SPMDs to define the “Data Quality Objectives” pertinent to the use of SPMDs. The results of this work should aid in regulatory acceptance of SPMDs for monitoring ambient organic contaminants.

PLATFORM PRESENTATION

Removal of Methyl Oleate from SPMD Extracts Using Normal-Phase SPE

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Analyte recovery from SPMDs coextracts interferences stemming from the LDPE tubing (polyethylene oligomers) and triolein impurities. The most problematic interference is methyl oleate, which is present in the final dialysate of a standard SPMD prepared with 95% triolein and concentrated to 1 mL at approximately 18 mg/mL. These high levels produce a substantially overloaded, shark-fin-shaped gas chromatography (GC) peak which can obscure co-eluting compounds, shifts analyte retention times, and elevate the baseline. Currently, an HPLC cleanup procedure based on molecular size-exclusion using gel permeation chromatography (GPC) is commonly employed to separate the methyl oleate from analytes. This method requires expensive equipment, is time-consuming, labor-intensive, and not entirely effective. In the current work, a normal-phase solid-phase extraction (SPE) method was developed utilizing a commercially available dual-zone restricted-access sorbent to separate methyl oleate from the 16 EPA priority-pollutant polynuclear aromatic hydrocarbons (PAHs) in a hexane matrix. In this technique, the SPMD dialysate is applied directly to the SPE cartridge and eluted with a hexane:methylene chloride (97:3) mixture to selectively remove methyl oleate while eluting PAHs. This specific removal of methyl oleate likely stems from polar interactions between the methyl ester groups on the ligand and methyl oleate. This method provides a simple and inexpensive normal-phase cleanup method that can be used to replace conventional GPC techniques for the enrichment of PAHs in SPMD extracts.

PLATFORM PRESENTATION

Investigation of Dissolved Polycyclic Aromatic Hydrocarbons in Waters of the Everglades

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Polluted runoff has been suggested as a major source of PAH contamination in waters of the Everglades. Environmentalists as well as community members have growing concerns about PAH contamination in the ecosystem because of toxic effects on the aquatic, terrestrial and human tissues. Also, agricultural chemicals from farmland and toxic materials from urban areas have severely impacted the aquatic ecosystem in south Florida. There is a lack of information about the spatial and temporal distribution of dissolved PAHs and their photoproducts. These pollutants of interest are difficult to measure by conventional means of sampling. Furthermore, a means of sampling and measuring ultra-trace levels of PAH photoproducts in the aquatic environment has not been reported. The contaminants of interest in this investigation were selected PAH quinone photoproducts and the priority pollutant PAHs. Two canals that are monitored by the South Florida Water Management District were selected for this SPMD investigation. These canals are south of the Everglades Agricultural Areas and lead into the Everglades National Park. Special "alligator-proof" housing devices were designed for the study. After the 28-day sampling period, the SPMDs were retrieved, dialyzed and analyzed for PAHs and photoproducts. The portion for the 16-priority pollutant PAHs were fractionated, separated and analyzed by GC-PID. The quinone photoproducts were analyzed, without further cleanup, by direct HPLC-UV analysis. No chromatographic interferences of co-dialyzed components occurred. The GC and HPLC methods, in conjunction with SPMD sampling, enable PAHs as low as 10ng/SPMD to be measured. The photoproduct detection limits are estimated to be in the microgram/SPMD range by this method. We determined that levels of PAHs and the photoproducts in the waters of these two canals were less than the low detection limits of this sampling and analysis method. We also screened the SPMD samples for organochlorine pesticides and found DDT and several other pesticides at ng/SPMD levels.

PLATFORM PRESENTATION

Toxicological Monitoring of a Simulated Oil Spill on the St. Lawrence River: Phytoremediation

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The St. Lawrence River is a major aquatic artery for the movement of petroleum products to the heartland of North America from the Atlantic Ocean. To evaluate the impact of oil spills on riverine ecosystems a simulated oil spill was initiated June 10, 1999, on an intratidal wetland site along the St. Lawrence River at St. Croix, QC, Canada. The randomized block experimental design consisted of four replicates of five different conditions: one site was non-oil treated and the other four sites were oiled and each given a different treatment: natural attenuation (no nutrients added), ammonium nitrate + tri-super phosphate (commercial fertilizer) + intact plants, ammonium nitrate + tri-super phosphate + cut plants, and sodium nitrate + tri-super phosphate + intact plants. Weathered Mesa light crude (12 L) was sprayed and manually raked into the top 2-3 cm of each treatment block (4 x 5m). Changes in toxicity of the experimental sites during weathering and degradation were monitored with SPMD-TOX. SPMD, a semipermeable membrane device collected and concentrated the oil products and Microtox[®] Basic Test, a microscale toxicity test, determined the changes in acute toxicity (TOX). SPMD units (12.5 cm) enclosed in protective cases were deployed at the water:sediment interface at 0, 1, 3, 5, 7, 11, 15, and 20 weeks and exposed SPMDs were retrieved after a one-week period. SPMD concentrated samples were directly diluted with organic solvents for toxicological analysis by Microtox. Changes over time in toxicity of the oil spill area were detected. The objective of this simulated oil spill was to determine the effectiveness of bioremediation with and without the presence of plants and to determine if petroleum contaminated freshwater wetlands can be restored to wild-type conditions. SPMD-TOX offered a rapid, sensitive, simple, and economical risk assessment of an oil spill.

PLATFORM PRESENTATION

The Use of Passive Samplers to Determine Soil Contaminant Levels and Monitor Changes in Contaminant Bioavailability with Aging

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Determination of the distribution of contaminants in soil may be one of the single most costly aspects in site assessments. Conventional determination of soil chemical concentrations typically involves lengthy solvent extractions and sample cleanup procedures which are usually time consuming and costly. A rapid sampling method using passive sampling techniques can provide a more thorough site assessment. Many efforts have focused on the use of passive sampling devices (PSDs; polymeric membranes filled with a sorbent) to determine aqueous phase chemical concentrations in aquatic systems. We have been pursuing their application in terrestrial systems, and have found them to be capable of accurately estimating soil chemical concentrations in six field studies. The PSD is sampling only the portion of contaminant either in the vapor phase or truly dissolved in the aqueous phase of the soil. As such, we have been successful in correlating PSD contaminant levels to soil concentrations. PSDs increase ease and speed of analysis, decrease solvent usage and overall cost, and minimize the transport of contaminated soils. Time and cost savings allow a high sampling frequency, providing a more thorough site characterization than traditional methods. We are investigating the use of PSDs to determine contaminant bioavailability due to the polymeric membrane and the fraction of contaminant being sampled. Thus far, accumulation in PSDs mimics that in earthworms and changes similarly with contaminant aging. Additionally, decreases in PSD uptake with aging correlate to decreases in soil toxicity (as measured using standardized earthworm toxicity assays).

PLATFORM PRESENTATION

Evaluation of Persistent Hydrophobic Organic Compounds in the Columbia River Basin Using Semipermeable-Membrane Devices

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Persistent hydrophobic organic compounds are of concern in the Columbia River because they have been correlated with adverse effects on wildlife. We analyzed samples from nine main-stem and six tributary sites spanning more than 700 miles of the Columbia River (Washington and Oregon) for polychlorinated dibenzo-*p*-dioxins, dibenzofurans, polychlorinated biphenyls, organochlorine pesticides, and priority-pollutant polycyclic aromatic hydrocarbons. Because these compounds may have important biological consequences at aqueous concentrations well below the detection limits associated with conventional sampling methods, we used semipermeable-membrane devices (SPMDs) to sample water. By compositing up to 15 SPMDs per sample, we achieved parts-per-quintillion detection limits. All of the compound classes investigated were prevalent within the basin, but concentrations of many analytes were highest in the vicinity of Portland-Vancouver, indicating that the Willamette subbasin – and perhaps the urban area in particular – is an important source of these compounds. Data collected during basin low-flow conditions in 1997 and again during basin high-flow conditions in 1998 indicate that in-stream processes – such as dilution by relatively clean inflows and flow through island hyporheic zones – may be important mechanisms for attenuating dissolved concentrations of hydrophobic compounds.

PLATFORM PRESENTATION

Semipermeable Membrane Devices (SPMDs) Used for Evaluation of Concentration Profiles of Pyrethroids in Ponds

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Semipermeable Membrane Devices (SPMDs) are thin layflat polyethylene tubes filled with triolein. The membranes will allow dissolved organic chemical compounds to pass the membrane while chemicals adsorbed to dissolved organic matter or to particulate matter will not be absorbed. SPMDs mimic the uptake of hydrophobic chemicals in aquatic organisms. A series of SPMDs were placed at intervals from the bottom to the top of two artificial ponds. 4 Pyrethroids, fenpropathrin, permethrin, esfenvalerate and deltamethrin were sprayed on the surface of the ponds and the membranes were left in the ponds for 2 months. Pyrethroids are hydrophobic insecticides; $\log P_{ow}$ of the experimental compounds being 4.6-6.2. The excretion rate of these compounds from SPMDs is so low compared to the uptake rate that in practice the pyrethroids will stay in the SPMDs even when the water concentration decreases. Concentration of pyrethroids in SPMDs from different depth reflects the concentration of pyrethroids in the water phase at these depths. Corresponding concentrations of pyrethroids in water and in SPMDs are used to evaluate a model for vertical dispersion of pesticide in the water column combined with sediment uptake by adsorption and pore water diffusion.

PLATFORM AND POSTER PRESENTATION

Monitoring of POPs in Odra River (Czech Republic) by Passive Methods (SPMD, DGT)

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The North Moravia (Czech Republic) region belongs to the most polluted regions in Czech Republic by POPs and heavy metals. Main sources of contamination are steel plants (POPs, metals), chemical factories (paper plant, plants for chemicals (POPs)), agriculture and forest industry (OCPs). New sources of contamination are going to appear (incinerator, power plants, oil combustion plant, local heating, etc.). There are main sources of drinking water in this region (dumps with cover water). All sources are subjected to periodical water quality testing and assessment responsible officials for drinking water management. The active sampling method is only used. Due to very slow concentration POPs and heavy metals and technical limitation to amount of sample treated common method was passive method of sampling used. The both Semipermeable Membrane Device (SPMD) for POPs and Diffusive Gradient Thin Film (for metals) methods were used as complementary method to the commonly method used. The pilot study of passive sampling was applied for Ostravice River along the whole stream passing through industrial region including one down stream. The drinking water source (Sance Dump) was also monitored and for these study these samples was considered as background. Wide scale of contaminants was monitored: PCBs, PAHs, PCDDs, PCDFs, OCPs and selected metals. Concentration of mentioned contaminants found in this study could reflect flooding episode in 1997. One of the most important factors was also studied. The main aim was looking for an influence of geogenic and anthropogenic background. Sampling experiments were performed in Wieliczka Salt Mine (Poland) in range mentioned POPs excluding metals. The pilot study brought basic experimental results as the base for method validation to be accepted in frame local legislation and monitored programmes with connection of principles of multivariate data analysis and active water management.

PLATFORM PRESENTATION

Considerations Involved with the Use of Semipermeable Membrane Devices (SPMDs) For Monitoring Environmental Contaminants

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Semipermeable membrane devices (SPMDs) are used increasingly on a global scale as samplers of organic contaminants. The devices can be used to detect a variety of lipophilic chemicals in water, sediment/soil, and air. SPMDs are designed to sample nonpolar, hydrophobic chemicals, and the maximum concentration factor achievable for a particular analyte is proportional to its K_{OW} . This generally limits the utility of the device to sampling compounds with $\log K_{OWs} > 3.0$. Cleanup of SPMD extracts for targeted analytes and for general screening by full-scan mass spectrometry does not differ greatly from approaches used for extracts from other matrices. However, SPMD extracts contain potential interferences that are specific to the membrane-lipid matrix. These include polyethylene waxes, oleic acid and methyl oleate. Processing of the SPMDs for analysis of sequestered contaminants begins with cleaning any biofilm, debris, and lipid off the exterior membrane surface, and extraction of contaminants via organic solvent dialysis through the intact polyethylene membrane. In a few situations where the method of detection or assay is selective and sensitive enough, this may be all the enrichment required. More often, however, the aforementioned interferences preclude analysis at this point. Potential interferences can be problematic when enrichment and/or fractionation procedures are limited to ensure retention of untargeted compounds for identification by full-scan mass spectrometry. A number of procedures have been developed or modified specifically for SPMD extracts to minimize interference from co-extracted SPMD related components. For example, high performance size exclusion chromatography and potassium hydroxide-treated silica gel cleanup methods have been developed for selectively removing lipid components, sulfur, and polyethylene waxes that would otherwise interfere with analysis of contaminant residues. In this presentation, we will identify specific approaches for handling and processing SPMDs and present effective approaches for addressing potential problems and analyzing the chemical residues sequestered by SPMDs. Ongoing research to enhance SPMD processing and analysis will be summarized.

PLATFORM PRESENTATION

A Holistic Approach for Assessing the Presence and Potential Impacts of Complex Mixtures of Environmental Contaminants

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Environmental contaminants seldom occur as single components, but rather are nearly always complex mixtures of a wide variety of chemicals. Currently, nearly all assessment approaches are limited in scope due to the complexity of the mixtures of contaminants in the environment. As an integral part of our continuing research in the development of environmental quality assessment approaches, we have developed a variety of broadly applicable integrative monitoring devices for use in defining the presence and potential impacts of a wide array of contaminants. The semipermeable membrane device (SPMD) has gained widespread use for sequestering hydrophobic chemicals from water and air; we are continuing development of the polar organic chemical integrative sampler (POCIS) for sequestering hydrophilic chemicals from water; and the stabilized liquid membrane device (SLMD) for waterborne ionic metals and the passive integrative mercury sampler (PIMS) for vapor phase or dissolved neutral mercury. This suite of integrative samplers forms the basis for a widely applicable approach for assessing the presence and potential significance of organism exposure to a broad spectrum of environmental contaminants. This holistic approach will be summarized and a proof-of-concept field deployment described. Future research will continue optimization of this holistic approach and development of additional integrative samplers, e.g., for volatile organic chemicals.

PLATFORM PRESENTATION

Using Semipermeable Membrane Devices for Estimating the Bioavailability of Organic Chemicals in Soil

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Soils are a complex environmental compartment with many physical and chemical attributes that modify the Bioavailability and toxicity of organic chemicals. Chemical exposure in soil toxicity tests and in ecological risk assessment of terrestrial systems is usually expressed as the total organic chemical measured following vigorous extraction with a nonpolar organic solvent. While this may be suitable for a specific test conducted with a single soil, it is erroneous to attempt to compare toxicity among different soils using total chemical as a measure of exposure. Possible alternatives to total chemical as a measure of organic chemical bioavailability and exposure include body residues in test organisms, soil extraction with selective solvents of varying polarity, and passive sampling devices (PSDs) as biological surrogates. Semi-permeable membrane devices (SPMDs) are efficient accumulators of lipophilic contaminants and offer potential as a biological surrogate in soil systems. The success of SPMDs in determining the bioavailability of organic chemicals in soil can be assessed by comparing chemical residue uptake in SPMDs with either physiological responses or chemical residues in soil-dwelling test organisms. The objective of this study was to compare organic chemical uptake kinetics and residues in earthworms (*Eisenia fetida*) and SPMDs exposed in artificial soil containing 1% or 10% peat as organic matter spiked with phenanthrene (PHE 0.31, 2.05, 3.10 mmol/kg, dry wt). Results suggest that bioavailable PHE, as assessed by mortality and body residues, varied dramatically with soil organic matter content. Although a steady state was not achieved, SPMDs could discriminate difference in PHE availability between treatments.

POSTER PRESENTATION

Determination of Equilibrium Constants (K_{SPMDs}) of Organic Compounds by Lipid Containing Semipermeable Membrane Devices (SPMDs) at Different Temperatures

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The effects of temperature on SPMD equilibrium constants (K_{SPMDs}) have not yet been explored and, consequently, the equations used to model the uptake of organic contaminants by SPMDs do not take into consideration the dependence on temperature. The purpose of our work was to quantify the effects of temperature on the K_{SPMDs} of Phenanthrene (Phe), p,p'-DDE, and 2,2',5,5'-Tetrachlorobiphenyl (TCB). The SPMDs used were a miniaturization of the standard, commercially available configuration. These samplers have a total mass of 0.21 g, of which 0.04 g is triolein. This represents a 4:1 polyethylene:triolein ratio. In each experiment, an SPMD was exposed to 1.6 L of water in a half-gallon jar. Exposures concentrations were below the published aqueous solubilities of each compound. The experiments were performed at two different temperatures: 18°C and 31°C. The 18°C-experiment was carried out inside an insulated stainless steel tank containing antifreeze/water, and the liquid in the tank was electrically cooled. The 31°C-experiment was performed in a heater/shaker. The results show that K_{SPMDs} decrease with an increase in temperature for all three test analytes. For DDE and TCB the K_{SPMDs} at 18°C are 24% and 46% higher, respectively, when compared to their 31°C values. For Phe the difference between the K_{SPMD} at 18°C and 31°C was the highest, 84%. Further experimentation is being performed at 8°C. So far, for Phe after 20 days the partitioning constant is higher ($K_{\text{SPMD}} = 38904.5$) than the equilibrium constants for the same compound at 18°C and 31°C. This verifies the trend of higher K_{SPMDs} at lower temperatures.

POSTER PRESENTATION

Progress Towards the Development of a Passive Sampler for Hydrophilic Organic Contaminants in Aquatic Environments

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Until recently, hydrophobic, bioconcentratable compounds have been the primary focus of most environmental organic contaminant investigations. There is an increasing realization that a holistic hazard assessment of complex environmental contaminant mixtures requires data on the concentrations of hydrophilic organic contaminants as well. This group of compounds includes the potent synthetic hormone 17 α -ethynylestradiol, which has been shown to contribute to induction of estrogenic activity in aquatic organisms exposed in environmental waters. A passive, *in situ* sampling approach (similar to that offered by the lipid-containing semipermeable membrane device [SPMD]) is needed to integratively concentrate trace levels of these complex mixtures of hydrophilic contaminants for the determination of time-weighted exposure levels and the assessment of toxicological significance of such exposures. Because some hydrophilic contaminant mixtures can be toxic even when individual components are at the ng/L level, performance criteria for a “hydrophilics” sampler should include analyte sampling rates of 0.5 L/d and a capacity for extended exposures (i.e., two weeks or more). To achieve this goal, we have investigated the use of several different types of hydrophilic membranes and sorbents. Test chemicals, used as model hydrophilic contaminants, were 17 α -ethynylestradiol, diazinon, and atrazine. Using a small prototype sampler (membrane surface area ~ 20 cm²) in relatively turbulent exposure water, a clearance volume of ~ 0.3 L/d was measured for 17 α -ethynylestradiol during an 18-day exposure period. An overall summary of progress to date will be presented.

POSTER PRESENTATION

Using SPMDs to Explore Causes of Amphibian Declines

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Incidence of amphibian deformities has increased in recent years, especially in the northern region of the United States. While a number of factors have been proposed as being responsible (e.g., contaminants, ultraviolet radiation, parasites), no single cause has been definitively established. In north-central Minnesota, some ponds have demonstrated high proportions of deformed frogs (nearly 80% in some species). Since the mid-1990s researchers have been attempting to find cause for these deformities in these ponds. Currently we are researching whether contaminants found at the sites are responsible for deformities by exposing native tadpoles to extracts of SPMDs. We used two sets of SPMDs that had been deployed for 30 days, one set in a reference and one in a contaminated site. Because many contaminants are photoenhanced, we also used UV radiation as a factor in our experiments. We found that the SPMD extracts were not acutely toxic to tadpoles, even at concentrations of up to 30x a daily dosage. Extracts from each of our two sites caused a decrease in embryonic deformity when exposed to UV light. Hatching success and tadpole weight after 10 days were lower in the contaminated site in the presence of UV light. We are currently attempting to determine whether there are differences in deformity rates among tadpoles reared for 45 days in the SPMD extracts from the two sites, with and without UV light.

POSTER PRESENTATION

Source Emission Survey Performed with Semipermeable Membrane Devices (SPMDs) in Various Environmental Sites (Indoor, Outdoor Air and from a Municipal Solid Waste Incinerator)

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SPMDs mimic passive diffusive transport of bioavailable contaminants through biological membranes and their partitioning between lipids and ambient levels. Although SPMD technology is becoming widely accepted, the literature provides little guidance on using them. In this paper we describe results of our attempts to use this kind of tool as air sampling system. A monitoring campaign was performed in order to evaluate the SPMD efficiency in sampling environmental air in various sites (indoor, outdoor and from a municipal solid waste incinerator), in comparison with conventional air sampling methodology. Contaminant residues sequestered in the SPMD were conveniently recovered by dialysis in organic solvent. Furthermore, air samples were concentrated by the two different methods (SPMD and conventional air sampling) for the evaluation of the best efficient recovery system. The extracts were tested in order to evaluate the potential toxic (Microtox®) and mutagenic effects. We also accomplished gas chromatography-mass spectrometry analyses in order to characterise the organic pollutants sampled. Results are very promising and in accordance to what expected. In conclusion, SPMDs showed a to be an excellent tool in assessing the presence of hazardous compounds, therefore this method could be of wide interest in assessing toxic contaminants in indoor and outdoor ambient for their capability in determining pollutant sources and relative levels at different locations.

POSTER PRESENTATION

Highway Environmental Impact Monitoring: SPMD Devices Application

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SPMD technique was developed for passive *in situ* monitoring of aquatic contaminants. Following, SPMD have been applied in various environmental applications, and also as highly efficient passive air samplers. Despite these promising results, few published data about this last application on air monitoring are available in literature. This method could be of wide interest in assessing toxic contaminants in indoor and outdoor environments for their ability in determining pollutant sources and relative levels at different locations. Our intention was to explore SPMD as passive air samplers in evaluating environmental impact of a highway using biological assays. Five sampling points representative of all ecosystems crossed by the highway were selected together with two control points (blanks). Standard SPMDs were deployed for three weeks in each site during the first sampling campaign (spring season, 2000) to investigate air quality related to automotive emissions. SPMD extracts have been used to assay air sample toxicity (Microtox[®]) and genotoxicity (Mutatox[®]). Bioassays gave interesting results and allowed the development of a risk assessment map, with increasing risk levels along the highway-investigated site. Furthermore, results of this study have highlighted the usefulness of toxicity and genotoxicity tests to assess health acute and chronic effects of bioavailable air traffic pollutants. In conclusion, SPMDs seem to provide an efficient tool for *in situ* biomimetic concentration of bioavailable environmental chemicals for biological tests. Moreover, while active air-sampling technology suffers from complex mechanical operation, passive air samplers are more attractive because of their simplicity. Furthermore, standard techniques often fail to detect trace levels of bioconcentrable contaminants and seldom recover enough residue mass for bioassays.

POSTER PRESENTATION

Characterization of a SEC System for the Fractionation of SPMD Dialysates

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Scientists at USGS-CERC have characterized the Phenomenex Phenogel SEC column using a 98:2 (V:V) dichloromethane:methanol mobile phase for the isolation of certain contaminants of interest in SPMD dialysates. This method is applicable to other environmental matrices, however, and has been tailored for the removal of lipids, polyethylene waxes, sulfur, and other co-extracted materials in SPMD dialysates. A calibration mixture consisting of, in order of elution, diethylhexylphthalate (DEHP), biphenyl, naphthalene, coronene, and sulfur is used on a daily basis to determine the relative retention of such materials on the column. Two alternative recommendations are given for “collect windows” beginning at either 50% or 70% of the difference in the retention volumes at the apices of the DEHP and biphenyl peaks. These “collect windows” are suitable for the collection of most analytes of interest. The retention volumes of over 110 different analytes and possible co-extracted interferences are reported and their appropriate “collect windows” given. Phenomena such as secondary adsorption of aromatic systems to the styrene-divinylbenzene column packing and shifts in retention volume relative to total analyte mass are described.

POSTER PRESENTATION

Potential for Photodegradation of PAHs Sequestered within an SPMD

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The potential for photodegradation of PAHs within the SPMD was investigated under various outdoor air and water sampling conditions. We investigated photodecomposition of sequestered PAHs during SPMD sampling and retrieval conditions, when exposed to filtered, reflected and direct sunlight may occur. SPMDs were spiked with priority pollutant PAHs and subjected to aquatic and atmospheric conditions for up to 7 days. Exposed SPMDs were compared to SPMDs kept in the dark under same sampling conditions. A facile analytical approach was developed for direct analysis of the PAHs and their photoproducts in SPMD dialysates. No extra clean-up steps were needed: co-dialyzed components that interfere with GC separation and detection did not affect the HPLC-UV chromatography or detection. PAHs known to be more susceptible to photodecomposition exposed to direct sunlight were degraded in atmospheric conditions. The amount of reflected sunlight entering the canister is of sufficient intensity to degrade the PAHs during air sampling period of 1 week. SPMDs deployed in pond water were not significantly affected by sunlight deployed at a depth of 2ft. When using the SPMD for PAH sampling, it is critical to preserve the sequestered PAHs during retrieval as well as air sampling. Formation of post-sampling degradation products and alteration of the sampled PAH patterns can occur if precautionary procedures are not taken.

POSTER PRESENTATION

Toxicological Risk Assessment of Environmental Waters: the Use of Microscale Monitoring – SPMD-TOX

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Waterborne chemical contaminants were assessed by a new tandem monitoring procedure (SPMD-TOX) that used microscale toxicity tests to detect chemical contaminants collected by a synthetic membrane device. This semipermeable membrane device (SPMD) mimics the passive sorption of lipophilic contaminants through biological membranes and concentrates the pollutants in a thin film of lipid (triolein) enclosed in polyethylene tubing. SPMD-concentrated samples were diluted with organic solvents for toxicological analysis by the Microtox Basic Test[®] and the Mutatox Genotoxicity Test[®] -- two microscale tests. Extracts were exposed to glowing luminescent bacteria in the Microtox Basic Test and to non-glowing (dark mutants) luminescent bacteria in the Mutatox Genotoxicity Test. The amount of light decrease in Microtox Basic Test indicated the acute toxicity (EC_{50}) of the sample and the amount of light increase in Mutatox Genotoxicity Test, with or without metabolic activation, indicated the genotoxicity (Yes-No) of the sample. Toxicological evaluations of samples from lentic and lotic systems were successfully made in <24 h by SPMDs, Microtox, and Mutatox used in combination. The SPMD-TOX offered a rapid, sensitive, simple, and economical risk assessment of our Nation's environmental waters.

POSTER PRESENTATION

Purification of 95% Triolein Prior to its Use in the Fabrication of Semipermeable Membrane Devices (SPMDs): Removal of Methyl Oleate and Oleic Acid Impurities

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A simple and cost-effective method has been developed for the purification of 95% triolein destined for use in SPMDs. Analytical problems resulting from residual methyl oleate and oleic acid impurities in dialysates (even after gel permeation chromatographic fractionation) can therefore be prevented. The purification method consists of repetitive (4X) partitionings of 95% triolein with methanol, followed by centrifugations. About 96% of the methyl oleate and virtually all of the oleic acid are removed; 89% of the triolein is recovered. The resultant triolein is of greater purity than the commercially available 99% grade, but costs only about 62% as much on a per-gram basis. Comparative testing will soon be performed for SPMDs made from triolein thus purified versus standardized SPMDs (made from commercially available 95% triolein). Will their sampling behaviors be alike?

POSTER PRESENTATION

Assessment of Indoor Airborne Organic Contaminants using Semipermeable Membrane Devices

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Aerial transport of organic contaminants occurs globally. Contaminants are removed from the atmosphere by particulate fallout, vapor phase solution, rainout and snowfall, and vapor phase sorption. Before these processes remove airborne contaminants, the chemicals are often transported great distances from the original pollution source. Consequently, airborne contaminants have the potential to adversely effect ecosystems and human populations far removed from the source of pollution. Because people spend the majority of their lives inside buildings where they may be exposed to airborne chemicals through infiltration and input from ventilation systems and from sources within the building, assessing the consequences of exposure to the chemicals present in indoor areas is of great importance. As part of a large project to determine the potential for adverse effects associated with human exposure to hydrophobic contaminants, we deployed semipermeable membrane devices (SPMDs) in indoor areas at selected sites along the Arizona/Mexico border. The samplers were deployed for 30 days in order to provide an integrated assessment of the airborne chemicals present in the indoor areas. Analysis of the sample extracts revealed the presence of a broad array of airborne chemicals, including, but not limited to, the DDT complex, chlorpyrifos, polycyclic aromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs). Contaminant residues ranged from trace levels to μg per sample quantities. The consequences of human exposure to this complex mixture of airborne chemicals are currently unknown.

POSTER PRESENTATION

Are SPMDs as Good as Mussels? A Comparison of the Green-Lipped Mussel (*Perna viridis*) and SPMDs for Monitoring Organochlorine Contaminants in Hong Kong Coastal Waters

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A comparison of mussels (*Perna viridis*) and semi-permeable membrane devices (SPMDs) was carried out at five sites, representing a gradient of contaminant concentrations, in Hong Kong coastal waters. Mussels, originally collected from a “clean” location, were deployed along with SPMDs at each site for 30 days. Analyses of chlorinated pesticides and polychlorinated biphenyls (PCBs) indicated that SPMDs have potential as monitoring tools, and to some extent can overcome the problems associated with mussels. However, in most cases, SPMDs failed to rank the sites in the same order as mussels in terms of contaminant concentrations. Nonetheless, in localities where mussels cannot survive – as shown at Kwun Tong in the present experiment - SPMDs may be valuable in providing an indication of potentially bio-available lipophilic pollutants.

POSTER PRESENTATION

Monitoring Dioxin Levels in Maine Rivers with Semipermeable Membrane Devices

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The Maine Department of Environmental Protection (DEP) currently monitors river dioxin levels through focusing on dioxin's bioaccumulation in fish. Recent state legislation mandates that by 2003, the levels of dioxin in the river downstream from an industrial facility are not to exceed the levels upstream from that facility. This thesis project seeks to fulfill the requirement of finding a suitable method for determining industrial facility compliance to this upstream-downstream law. Semipermeable membrane devices (SPMDs) provide an alternative dioxin monitoring method that circumvents many of the problems present in the current fish method. Over the course of two field seasons, we will assess the feasibility of using SPMDs to monitor dioxin levels in Maine rivers. The 1999 field season focused on developing viable field and laboratory SPMD methods while the 2000 field season looks to applying these methods to upstream-downstream sites. The laboratory methods developed in the 1999 field season achieved success as demonstrated by surrogate recoveries falling within the acceptable ranges of EPA Method 1613B. Moreover, chromatograms obtained through high-resolution gas chromatography / high-resolution mass spectrometry (HRGC/HRMS) indicate that both toxic and non-toxic dioxin congeners have been collected from the river by the SPMDs.

POSTER PRESENTATION

Uptake and Release Kinetics of Selected Organochlorines and PAHs by Mussels and SPMDs

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Uptake and release kinetics of selected PAHs and organochlorine pesticides were studied in semi-permeable membrane devices (SPMDs) and mussels (*Perna viridis*) deployed in a static daily renewal system. Organic contaminants in the experimental tanks were distributed between the seawater dissolved phase and a particulate phase, the latter being composed chiefly of unicellular green algae (*Dunaliella tertiolecta*) which were used to feed the mussels. Calculation of kinetic constants for mussels indicated that uptake from the particulate phase was significant for contaminants which tend to partition in that phase. Despite the fact that, by definition, SPMDs sample only dissolved compounds, most of the tested contaminants were taken up at rates comparable to those for mussels. Conversely, contaminant elimination took place much more rapidly in mussels, implying that SPMDs are better candidates for detecting episodic discharge of organic contaminants.

POSTER PRESENTATION

Calibrating the Uptake Kinetics of Semipermeable Membrane Devices in Water: the Impact of Hydrodynamics

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Lipid-containing semipermeable membrane devices (SPMDs) present a monitoring method that is convenient for continuous passive, *in situ*, monitoring of bioconcentratable organic contaminants in a watercourse. At present time, only few sampling rate data are available for the estimation of ambient contaminant concentrations from analyte levels in exposed SPMDs. In order to characterize the effect of water flow conditions on the uptake kinetics, SPMDs were exposed in a chamber connected to a continuous-flow system over a time period of 20 days at constant water concentrations and at three flow velocities. During exposure, membrane devices were sampled at time intervals and their contents analyzed to determine concentrations of selected organochlorine pollutants. The release of deuterated anthracene spiked to the SPMDs prior to exposure was used as independent measure of the exchange kinetics between SPMD and water. Static exposures were also conducted to measure the partition coefficients of the organochlorines between SPMD compartments. A kinetic model for contaminant accumulation incorporating both aqueous film and polyethylene film mass transfer was fitted to data from exposure studies. The data suggest hydrodynamic conditions may control the accumulation of many chemicals in SPMDs.